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Electronic structure and properties of the superconductor $\text{Pb}_2\text{Sr}_x\text{La}_{2-x}\text{Cu}_2\text{O}_{6+\delta}$

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The electronic structure of the cuprate superconductor $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$ has been calculated within the local density approximation with the augmented spherical wave method. The results feature a band crossing the Fermi level, being mostly of copper oxide character, with a slight admixture of lead oxide. The admixture of Pb character in the conduction band is in agreement with NMR measurements.

1. Introduction

Since the discovery of the first high- T_c materials many attempts have been made to synthesize new materials which also have a very high superconducting transition temperature. Recently, the structure of one of these new materials, $\text{Pb}_2\text{La}_{2-x}\text{Sr}_x\text{Cu}_2\text{O}_{6+\delta}$, has been published [1]. This compound can be derived from the class of superconductors synthesized by Cava et al. [2], with general formula $\text{Pb}_2\text{Sr}_2\text{ACu}_3\text{O}_{8+\delta}$, where A is a rare earth element. These materials feature a CuO_2 double layer. The present compound can be derived from the “Cava” compounds by removing one CuO_2 and one A layer.

The phase diagram of the compound turns out to be complicated. For zero doping, $\delta=0$ and $x=1$, the material probably is a semiconductor. For $x=1$, the material becomes superconducting on increasing δ with an almost δ -independent T_c of approximately 33 K. Hall measurements are consistent with the expected [1] hole character of the charge carriers [4]. If δ approaches 0.2, T_c drops fast and becomes zero for $\delta=0.2$. The material does not form with δ between 0.2 and 1.4. On oxygen annealing the $\delta=0$ phase, δ jumps to 1.4, forming an insulating phase [4].

In order to make a step forward in understanding both the similarities and differences with the known high- T_c materials, a series of NMR experiments has been performed, described in an accompanying paper, and the bandstructure has been calculated within the local density approximation. From the NMR experiments it is possible to gain information on the hyperfine coupling constant of lead, which in turn provides an estimate of the admixture of Pb 6s character at the Fermi level. Also, bandstructure calculations introduce the possibility of comparing results for e.g. the hyperfine coupling constant, with results obtained within the framework of the local model of Mila and Rice [5].

The calculations have been performed for the $x=1$, $\delta=0$ stoichiometry. Though this material is a semiconductor, we expect, based on the experience with other copper oxide superconductors [6] that within a rigid band picture the main conclusions may be extended to slightly doped superconducting systems. Attention will be focused specially on the possible metallicity of the lead oxide layers, separating the CuO layers. Also, the importance of the $\text{Cu } d_{z^2}$ orbital will be discussed, as in some explanations of high- T_c superconductivity it plays a crucial role [7,8].

The paper is organized as follows. In section 2 we will briefly describe the structure of the system, and

present the details of the bandstructure calculation. The results of the calculation will be presented in section 3. In section 4, the implications of the calculations for nuclear magnetic resonance (NMR) are discussed.

2. Structure and bandstructure calculations

2.1. Structure

The crystal structure [1] shows the material has many similarities with the compounds reported by Cava et al. [2]. A feature which positions the compound in a different class, is the presence of a CuO_2 single layer instead of a double layer.

In fig. 1 the unit cell of $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$ is shown. The crystal structure can roughly be described in the space group Cmmm. Benschop et al. [1] showed that some oxygen atoms deviate from high symmetry positions in this space group. A better space group representation was found to be Pman in which the oxygen atoms in the lead layer were shifted in the b -direction leading to an irregular five fold coordina-

tion of lead. Also the oxygen atoms in the CuO_2 layer were shifted somewhat in the c -direction similar to the oxygen atoms in the tilted octahedra in La_2CuO_4 . The shift of the oxygens in the Sr, La layer is not significant. The Cu atom in the vacancy layer is linearly coordinated by the oxygens in the PbO layer.

The Sr and La atoms are randomly distributed over one crystallographic position with partial occupations. To account for this we used in the calculations space group P2/m11 , i.e. P2/m with unique a -axis, and placed the Sr and La atoms in different Wyckoff positions in each Sr, La layer. This non-standard setting was used since it is customary to choose the c -axis perpendicular to the copper–oxide planes in the high- T_c materials. The unique angle was taken to be 90° .

In table 1 the atomic positions used in the calculations are given, using the positional data from the refinement in Cmmm. Included in parentheses are the positions of the displaced oxygen atoms in the PbO layer which were used in a second calculation. The shifts were taken from refinement in Pman. Again the calculation was performed in P2/m11 .

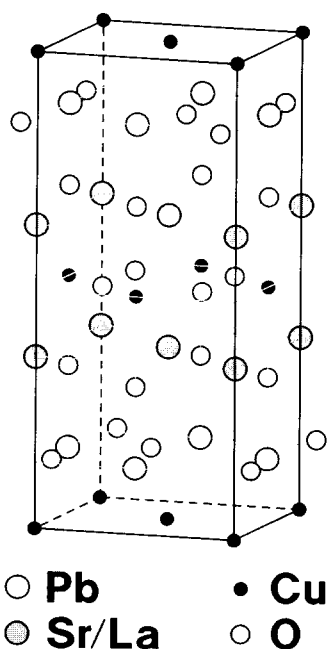


Fig. 1. Unit cell of $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$. The oxygen atoms in the PbO plane are displaced from their $(0, 0, z)$ and $(\frac{1}{2}, \frac{1}{2}, z)$ positions.

Table 1

Crystal coordinates used in the bandstructure calculation

Atom	Wyckoff position ^{a)}	x	y	z
Pb(1)	2m	0.0000	0.5000	0.3603
Pb(2)	2n	0.5000	0.0000	0.3603
Sr	2m	0.0000	0.0000	0.1384
La	2n	0.5000	0.5000	0.1384
Cu(1)	1d	0.0000	0.0000	0.5000
Cu(2)	1h	0.5000	0.5000	0.5000
Cu(3)	1c	0.0000	0.5000	0.0000
Cu(4)	1b	0.5000	0.0000	0.0000
O(1)	4o	0.2500	0.2500	0.0000
O(2)	2n	0.0000	0.5000	0.1864
O(3)	2m	0.5000	0.0000	0.1864
O(4)	2m	0.0000	0.0000(−0.08)	0.3509
O(5)	2n	0.5000	0.5000(0.58)	0.3509
Va(1)	1e	0.5000	0.0000	0.5000
Va(2)	1f	0.0000	0.5000	0.5000
Va(3)	4o	0.2500	0.2500	0.2700
Va(4)	4o	0.2500	0.2500	0.7300
Va(5)	4o	0.2500	0.2500	0.4309
Va(6)	4o	0.2500	0.2500	0.5691

^{a)} Spacegroup: P2/m11 ; $a = 5.3119 \text{ \AA}$, $b = 5.4140 \text{ \AA}$, $c = 12.629 \text{ \AA}$.

2.2. Bandstructure calculations

Bandstructure calculations for both structures with and without displacements of O(4), O(5) were performed using the augmented spherical wave (ASW) method, as described by Williams, Kübler and Gelatt [9]. Exchange and correlation effects were treated within the local density approximation as given by Hedin and Lundqvist [10]. Scalar relativistic effects were included as described by Methfessel [11]. In the calculations the s, p and d atomic wave functions were taken into account explicitly for Pb, Cu, La and Sr, and the 2s and 2p functions for O, whereas the f functions for Pb, Cu, La and Sr and the d functions for O were treated in perturbation theory. After each cycle in the iteration process, the core states were recalculated. No spin-orbit coupling was included.

To treat the large empty space in the crystal structure appropriately, empty spheres were included in the oxygen vacancy layer, and between the different layers. The positions are tabulated in table 1.

An eight k -point sample in the irreducible zone was used to carry out the Brillouin zone integrations in the course of converging the potential. For calculating the density of states, a 24 point integration was used.

3. DOS and bandstructure

In figs. 2 and 3 the total density of states, and partial densities of states for several atoms are shown. It is clear, that the local density calculation predicts

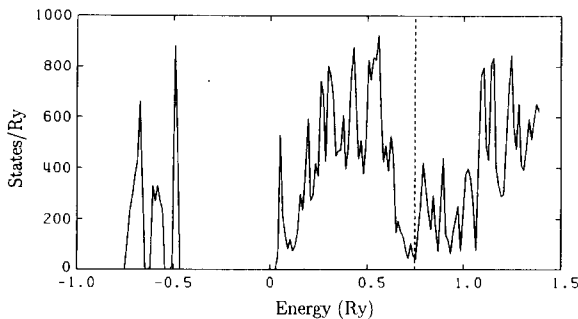


Fig. 2. Total DOS of $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$. Energies are in Ry (13.6 eV).

a metallic ground state for the undoped $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$. This is in contradiction to conductivity measurements [4], which indicate that the $\delta=0$ compound probably is a semiconductor. We expect, however, that the doped, superconducting compound can be described by the calculated bandstructure [6].

The contribution to the DOS below E_F of the La and Sr atoms is marginal. This is in agreement with the ionic nature (Sr^{2+} and La^{3+}) of these atoms in $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$. Also, a significant difference between the copper atoms in the vacancy layer and the copper atoms in the copper oxygen layer is present. The atoms in the vacancy layer do not contribute at all to the DOS above E_F , which shows that the valence state of these atoms is d^{10} . This is in good agreement with XAS measurements on $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$ [12], where the presence of peaks near 994 eV strongly suggests the presence of Cu^+ in a d^{10} state. From the chemical point of view, the linear coordination of copper is also a strong indication of the mentioned singly oxidized state for copper. In a related compound, $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$, such a vacancy layer is present as well. Bandstructure calculations [13] on this compound indicate, in analogy with the results for the present compound, that the copper vacancy layer is characterized by monovalent copper.

In agreement with the common lore that the conduction band in high T_c s consists of CuO_2 bands, the largest fraction of the DOS close to E_F is due to the $\text{Cu } 3d_{x^2-y^2}$ and $\text{O}(1) 2p$ orbitals, and only a small amount of PbO character is involved. The s-orbital of the copper atoms is almost empty, and integration of the d-band DOS results in an effective valence state of copper of d^9 , in agreement with the proposed double charge. A striking fact is the presence of a sharp peak in the DOS just above E_F . This peak consists mainly of $\text{Pb } 6s, 6p$ and $\text{O } 2p$ orbitals. If we introduce in the calculation the slight displacements of the oxygen atoms in the PbO layer, as suggested by the X-ray diffraction data, this peak is somewhat smeared out. Due to this effect some PbO character is added to the DOS at E_F , and the density of states at E_F is increased slightly.

In fig. 4 we present the bandstructure of $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$ (without oxygen displacements). The most distinctive feature is, near E_F , the presence of

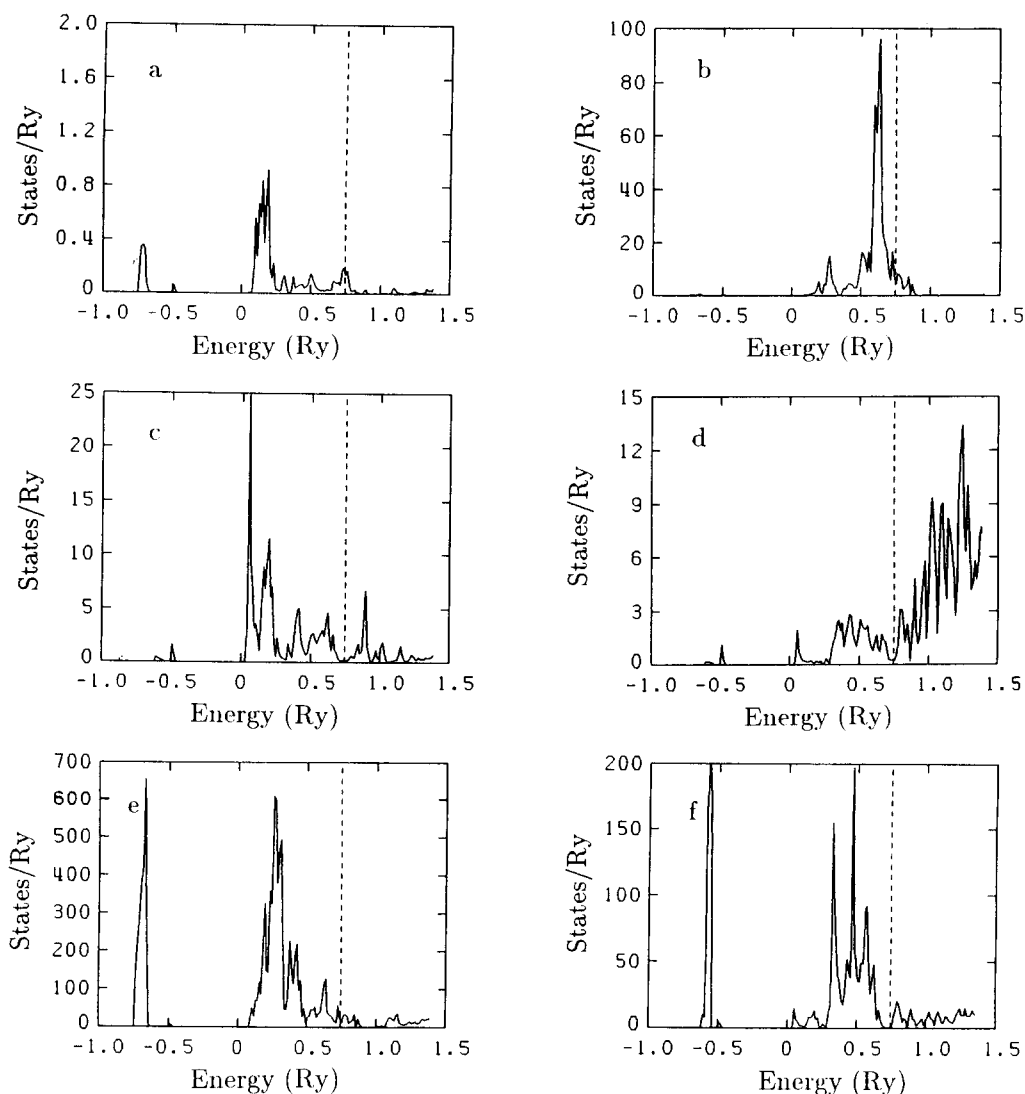


Fig. 3. Total DOS and partial densities of states for Cu and Pb. (a) and (b) partial 4s and 3d DOS of Cu(2); (c) and (d) partial 6s and 6p DOS of Pb; (e) and (f) total DOS of O(1) and O(4, 5).

very narrow bands. The bands straddle the Fermi level, and have mostly Cu $d_{x^2-y^2}$ and O(1) p_x and O(1) p_y character. Still, a significant amount, about 1.5%, of Cu 4s character is mixed in. Even more, about 5%, of Pb 6s and O(4, 5) p character is admixed. Due to the fact that the compound is slightly distorted from tetragonal symmetry, also a small amount of d_{xy} character is hybridized. No substantial amount of copper 3d_{z²} character is observed at the Fermi level. Just above the Fermi level lies a band, originating from lead 6s, 6p and oxygen 2p or-

bitals, which is more or less parabolic, reflecting the free electron character of this band. As mentioned before, these bands are quite sensitive to small displacements of the oxygen atoms in the PbO layer. A small displacement already results in a fairly large increase in the admixture of PbO character in the CuO band crossing the Fermi surface.

Still higher in energy above the Fermi level, above 1.1 eV, bands consisting mainly of Pb 6p and a small amount of Pb 6s character are found. This is consistent with the calculations on $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ [13],

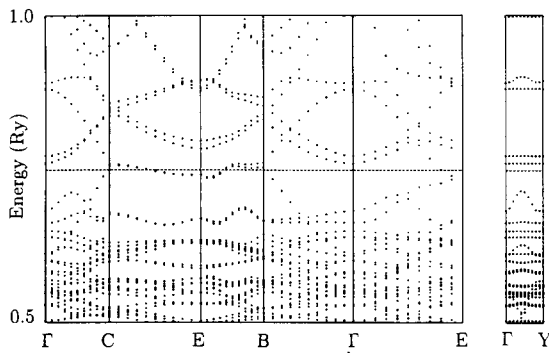


Fig. 4. Energy bands for $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$. Note that the unique axis used in labelling the high symmetry points is the, for monoclinic symmetry conventional, c -axis, not the a -axis used in the text.

where also predominantly Pb 6p character is found in the bands from 1 to 4 eV above the Fermi level.

The highly two-dimensional character of the compound is reflected in the fact that the dispersion in the k_z direction (most prominently in going from Γ to Y) is nearly flat. Only the band just below the Fermi level, which is formed from a hybridization of Cu 4s and $3d_{z^2}$, and Pb 6s orbitals, shows some curvature. This band may play an important role in the well-doped systems. On electron depletion, in a rigid band picture this energy band may cross the lowered Fermi level and consequently give rise to a “two band” picture, where one band is originating mostly from the Cu $3d_{x^2-y^2}$ orbital, and the second from Cu 4s and Cu $3d_{z^2}$.

Our findings for the present compound are in line with the trends elaborated by Khomskii and Di Castro et al. in refs [15] and [16], where it is shown that for many compounds a higher hole occupation for the d_{z^2} orbital is concomitant with a decrease of T_c . The present compound becomes superconducting on a slight increase of the oxygen content; the doping level needed for the $3d_{z^2}$ orbital to gain a substantial weight at E_F , corresponds to $\delta \approx 0.18$. For this high doping level, T_c is indeed significantly suppressed, or may even be zero.

An interesting question arises as to the importance in the superconducting properties of the $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$, of admixture of the wavefunctions from the PbO layer to the copper-oxide layer. For $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, there are indications that a slight portion of TlO character is present at the Fermi sur-

face. Both bandstructure [17,18] and simple cluster calculations [19,20] show a non-negligible amount of Tl-s character at E_F . From NMR-measurements on the Tl nucleus in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ [20] also evidence is obtained that the thallium oxide layer contributes to the density of states at the Fermi level. For Bi the situation is less clear, though there seems to be a consensus now that the BiO layer gives no contribution to the density of states at the Fermi level [21]. Therefore, it is tentatively concluded from this that the importance of metallicity in the layer separating the copper-oxide layers is marginal.

4. NMR

With respect to NMR, $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$ displays characteristics similar to the Tl-based copper-oxide superconductors. In the latter compound, the CuO_2 layer is bridged via the apex oxygen atom with the TlO layer, whereas in the present compound the CuO_2 layer is bridged with the PbO layer. In the Tl based compound, the Tl 6s orbital is slightly hybridized with the copper $3d_{x^2-y^2}$ orbital, due to which the Tl nucleus is very sensitive for dynamic effects in the copper-oxide layer [19].

Because from the calculations it is clear that for the present compound some Pb 6s character is present at the Fermi level, also ^{207}Pb NMR may provide important information on e.g. the spin dynamics in the copper-oxide layer in $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$.

The strength of the coupling of the nuclear spins with the electronic system is governed by the hyperfine coupling constant A . If the atomic Fermi contact

Table 2

Densities in states/eV (per formula unit) at the Fermi level. Only entries with contributions larger than 0.005 are given

Atom	Character	No states eV
Cu(3), Cu(4)	s	0.021
Cu(3), Cu(4)	$d_{x^2-y^2}$	0.953
O(1)	s	0.059
O(1)	p_x, p_y	0.540
Pb(1), Pb(2)	s	0.023
Pb(1), Pb(2)	p_x, p_y	0.038
O(4), O(5)	s	0.008
O(4), O(5)	p_x, p_y	0.120

term A_{Pb} is known, the following approximation for the hyperfine Fermi contact coupling constant A can be made:

$$A \approx A_{\text{Pb}} \langle |u_k|^2 \rangle E_F. \quad (1)$$

Here u_k is the contribution of the s-wave function of lead in the total wavefunction, and the average is taken over the Fermi surface. In this approximation, we have neglected the contributions which may arise due to admixture of a relativistic lead $P_{1/2}$ term, which also has a non-zero value at the nucleus. Effects due to core polarization, which are expected to be small because we deal with s and p electrons only, are neglected as well [23]. The same approach was used in a simple cluster calculation for approximating the hyperfine coupling constant in $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [19], where it proved to be quite satisfactory.

If the atomic contact term is taken from a Dirac-Fock calculation [22], A_{Pb} equals 56791 MHz, and a value for A of roughly 115 MHz is obtained. The number obtained is a factor of almost 2 larger than the experimental result, which amounts to 53 MHz.

From the partial densities of state at the Fermi level the zero frequency susceptibility $\chi(0)$, a quantity important in determining the Knight shift, can be computed. Within the free electron gas approximation

$$\chi(0) = \mu_B^2 \times D_{E_F}, \quad (2)$$

where μ_B is the Bohr magneton and D_{E_F} is the total density of states at the Fermi level. Putting in the numbers from table 2, a susceptibility of 1.0×10^{-4} emu/mol is obtained. This is a factor of 3 lower than the observed susceptibility (3.0×10^{-4} emu/mol) for a lightly doped sample ($\delta \approx 0.1$) [3].

The small discrepancy with experiment can only partially be explained by the displacement of the oxygen atoms in the PbO layer. This displacement increases D_{E_F} , thus resulting in a susceptibility of $\chi(0) = 1.4 \times 10^{-4}$ emu/mol. At the same time, A_{Pb} increases to a value of 125 MHz. Still, in view of the approximations made (the local density approximation itself and, e.g., the neglect of the enhancement due to electron-phonon interaction), the result of this ab-initio calculation may be considered as rather good.

Though the hyperfine constant A , calculated from the partial density of lead s-states at the Fermi level,

is too large, another important indication is obtained from NMR that indeed Pb s character is present at E_F . The transverse relaxation time T_2 has been measured in $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$, and is found to be roughly 200 μs , independent of temperature. This relaxation time is much smaller than expected on the basis of pure dipolar interaction – which gives a T_2 of about 4 ms. The partially occupied lead s-states however give rise to a kind of RKKY interaction between the nuclear spins, which has been described in ref. [20] in a localized model. A very slight anisotropy in the susceptibility of the PbO layers is then enough to obtain an interaction between the nuclear spins of the form

$$\mathcal{H}_{12} = I_1 \cdot \mathcal{A} \cdot I_2, \quad (3)$$

which describes the polarization of nuclear spin I_1 due to nuclear spin I_2 via the conduction electrons.

5. Conclusions

The ASW bandstructure calculation within the local density approach displays a metallic ground state for the undoped $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$. This is a deficiency which all LDA-based calculations have in common: a metallic ground state is predicted, whereas the system is a (antiferromagnetic) semiconductor. It is assumed, however, that the calculations are still applicable to the slightly doped systems.

The results feature a substantial amount of Pb 6s and Cu 4s orbital character at the Fermi level, besides the expected large amount of Cu $3d_{x^2-y^2}$ character. This observation is in agreement with NMR measurements. The PbO layer separating the superconducting CuO layers can therefore be considered as metallic, in which respect $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$ resembles $\text{Ti}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, for which compound also evidence is found for an admixture of TiO character at the Fermi level.

The calculations show a completely occupied Cu $3d_{z^2}$ orbital, indicating that this orbital does not play an important role in the slightly doped system. Within a rigid band picture, only at higher doping levels ($\delta \approx 0.18$) a second band with considerable $3d_{z^2}$ character crosses the Fermi level. As the critical temperature for this doping level is below the maximum T_c , or even zero, this is consistent with the

general trends for the high- T_c superconductors.

Finally, an attempt is made to calculate properties such as the Pauli susceptibility and the hyperfine coupling constant. The results are a factor 2 off the experimental values, which is quite good in view of the approximations made.

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